

Infrared Study of Polypropylene

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INTRODUCTION

Since the recent introduction of polypropylene into the polymer field¹ studies have been reported regarding the physical and chemical properties in this polymer. Some of these studies²⁻⁴ contain a limited amount of infrared data, but a more thorough investigation is required. This paper reports the results of our recent infrared studies.

Polypropylene is said to consist of an isotactic phase and an atactic phase. The isotactic phase has been assumed to be mostly crystalline whereas the atactic phase is considered to be mostly amorphous. Among the bands in the infrared spectrum, several have been assigned to each of the two phases present. Since the atactic phase and the isotactic phase give rise to their own characteristic absorptions, three objectives were considered in this portion of the study.

The first objective was to show that it is possible to distinguish clearly, by infrared, the atactic and the isotactic phases. The next objective was to show whether an infrared method could be developed by which the ratio of isotactic to atactic content could be determined rapidly and accurately, and thirdly, to ascertain whether the atactic phase was similar to the amorphous phase.

In connection with this portion of the study, the spectra of the 100% isotactic sample was also recorded during heating to 180°C. under nitrogen (the melting point of polypropylene is 165°C.) and then during the subsequent cooling period. This was done to show the effect of crystallinity.

The second portion of this study consisted of experiments in which the formation of hydroperoxides and hydroxyl- and carbonyl-containing oxidation products were followed by recording the spectra during accelerated oxidation.

Finally, the type of unsaturation found in polypropylene was also determined and confirmed by chlorination of a sample.

EXPERIMENTAL

The samples selected for the study of these phases were: (1) a highly isotactic (taken to be "100% isotactic") sample extracted with heptane then ether; (2) a commercial atactic sample (Hercules X10029-28-1); (3) a laboratory-prepared "100% atactic" sample (obtained by extracting a sample of polypropylene, made by the Ziegler method, with acetone and precipitating the atactic material with methyl alcohol); and (4) a chlorinated sample of atactic polypropylene (prepared by passing chlorine gas through a hot carbon tetrachloride solution of polypropylene).

All the spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer; NaCl optics were used.

RESULTS AND DISCUSSION

Atactic and Isotactic Phases

The significant differences in the characteristic spectra of "100% isotactic" and "100% atactic" polypropylene are shown in Figure 1.

As can be seen in Figure 1, the absorption bands in the 100% isotactic spectrum at 1366, 1330, 1305, 1295 (shoulder), 1258, 1220, 1103, 1045, 995, 938, 895, 842, and 810 cm^{-1} either become extremely weak or are eliminated in the spectrum of 100% atactic polypropylene (Curve B); this indicates that these bands are sensitive to isotacticity in polypropylene. The strong band in the 100% isotactic spectrum (Fig. 1, Curve A) at 1168 cm^{-1} with a shoulder at 1153 cm^{-1} shifts its band head (i.e., frequency where maximum absorption occurs) to ca. 1154 cm^{-1} in the 100% atactic spectrum. Actually what was the shoulder on the isotactic band at 1168 cm^{-1} becomes the main band head at 1154 cm^{-1} in the atactic spectrum. This band is discussed further below.

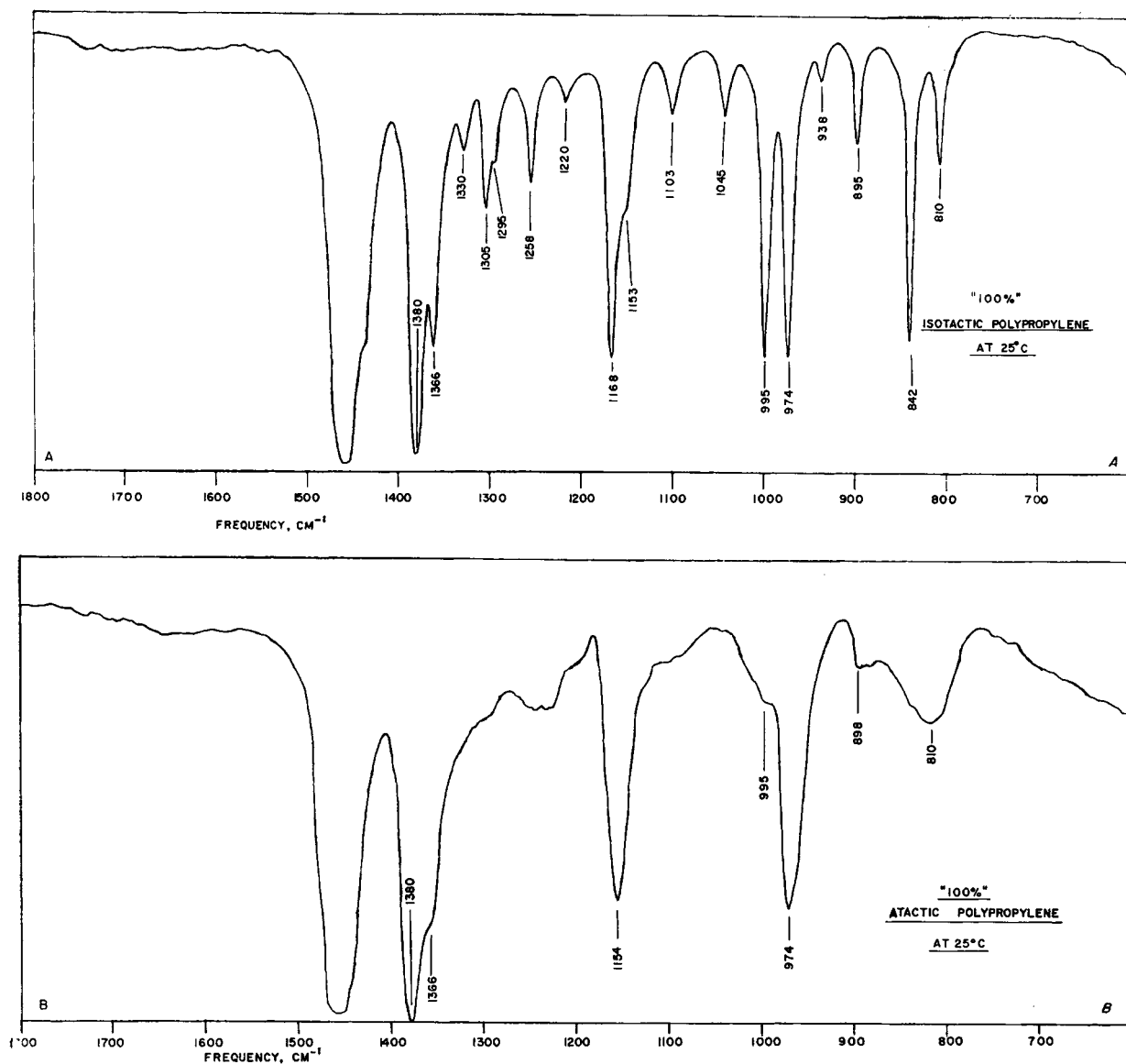


Fig. 1. Spectra of (A) 100% isotactic polypropylene at 25°C.; (B) 100% atactic polypropylene at 25°C.

The extreme similarity of the 100% atactic (at 25°C.) spectrum with that of the molten isotactic, which is considered amorphous at this point (i.e., at 180°C.) is shown in Figure 1 (Curve B) and Figure 2, (Curve A).

Since these spectra are similar, it may be said that the 100% atactic spectrum represents a completely amorphous material.

In the spectrum of commercial atactic polypropylene (Fig. 2, Curve B) it is evident from the intensity of the bands at 898, 888, 842, and 810 cm^{-1} , as well as the weak band at 995 cm^{-1} , that a significant amount of isotactic material is still present.

Quantitative Determination of Isotacticity

In the course of this study, several samples of the extracted matter from various commercial polypropylenes were subjected to infrared analysis. The extracted matter was obtained during the determination of the atactic and isotactic content by a generally accepted method described by Russell.⁶ Briefly, the method consists of a hot heptane and/or ether extraction in a vacuum-jacketed Soxhlet extraction apparatus for a specified period of time ranging from 6 to 24 hr. The weight ratio of extract to starting material gives the atactic content.

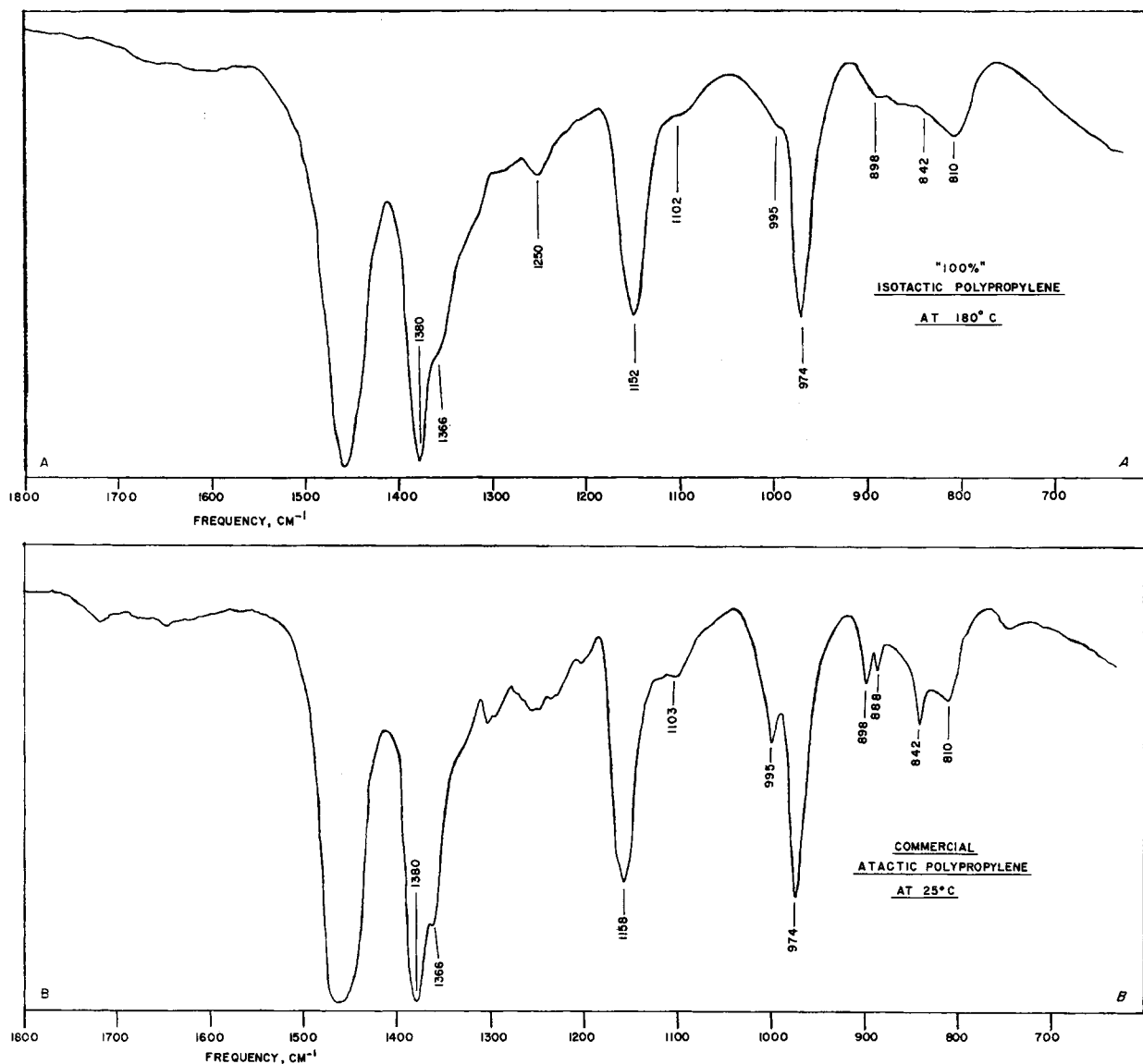


Fig. 2. Spectra of (A) 100% isotactic polypropylene at 180°C.; (B) commercial atactic polypropylene at 25°C.

It was surprising to find that the heptane-extracted matter contained a significant amount of isotactic material, probably of low molecular weight. The ether-extractable material consisted of stabilizers and other unidentifiable matter. Since this extractable matter is weighed and considered to be all atactic material (which apparently it is not), it is probable that the extraction method yields low results for the isotactic content. These findings suggested that an infrared method by which the ratio of atactic to isotactic content could be determined should be further studied.

Heinen⁵ has used the ratio of the 1171- cm^{-1} band to the 846- cm^{-1} band as a means of measur-

ing crystallinity. The "temperature-indifferent 1171- cm^{-1} band" used as an internal standard in his work appears as a single absorption band. Although the 1171- cm^{-1} band appears at 1168 cm^{-1} on our instrument, it is essentially at the same frequency. However, we have found that the 1168- cm^{-1} band has a shoulder at ca. 1152 cm^{-1} that is difficult to resolve. In Figure 3A, the 1168- cm^{-1} band is shown from different samples containing from 0 to 100% atactic material. The displacement of the 1168- cm^{-1} band by the 1156- cm^{-1} band (originally the shoulder), together with the simultaneous decrease in the extinction coefficient (absorbance/cm.) from 118 to 51.4 can be

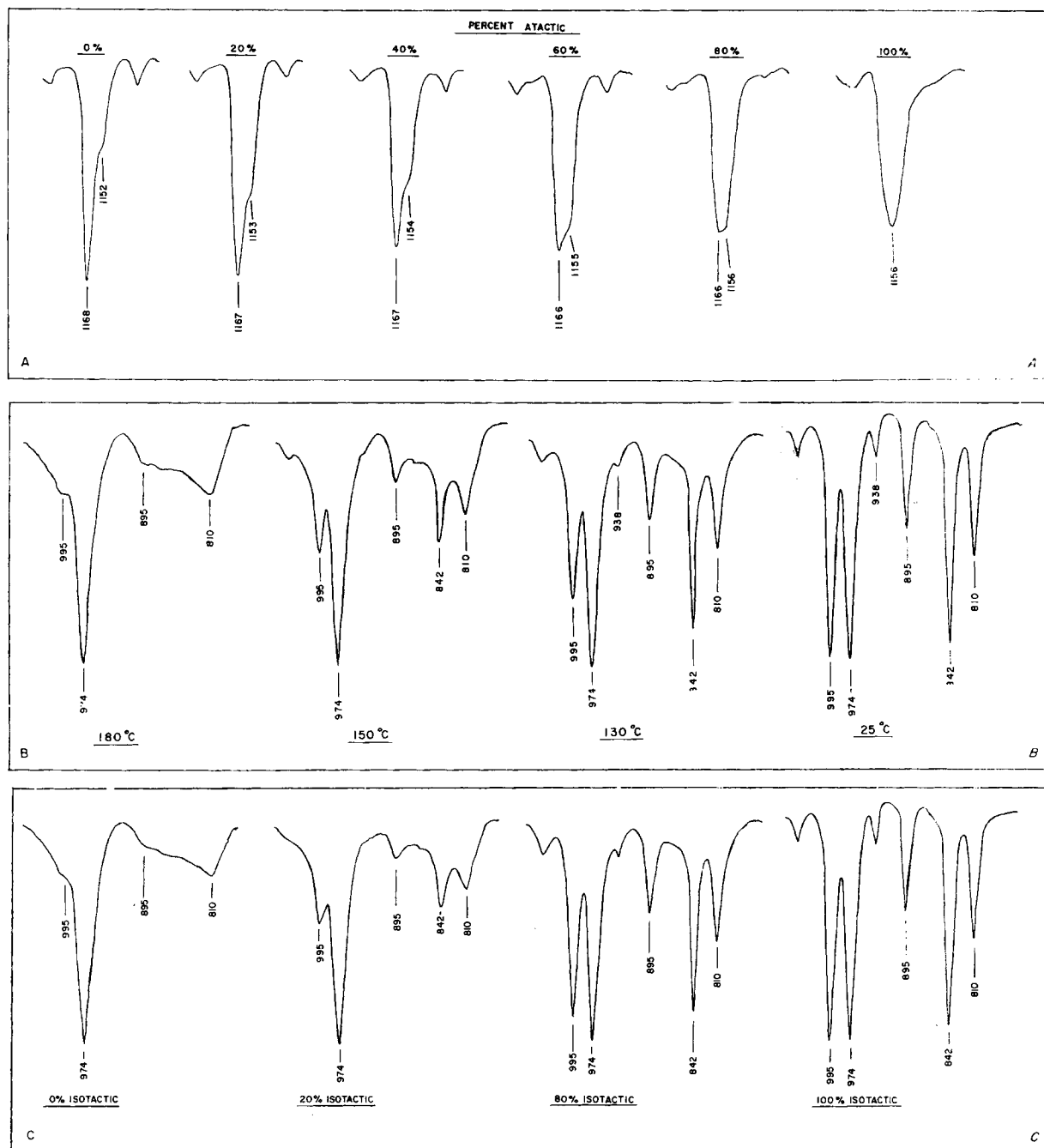


Fig. 3. Spectra showing (A) displacement of the 1168-cm.⁻¹ band by the 1156-cm.⁻¹ band due to change in atactic content; (B) 1050-750 cm.⁻¹ region of isotactic polypropylene while cooling from 180°C. to 25°C.; (C) 1050-750 cm.⁻¹ region of four laboratory-prepared standards of known isotactic content.

clearly seen. We believe, therefore, that Heinen's method for determining crystallinity should be used with due regard for these facts.

Of particular interest with regards to an infrared method are the bands at 974 and 995 cm.⁻¹. In the 100% isotactic spectrum both bands are of the

same intensity, whereas in the 100% atactic spectrum, the 995-cm.⁻¹ band is only a shoulder, while the intensity of the 974-cm.⁻¹ band remains the same.

Although there are other absorption bands which are sensitive to the isotactic and atactic phases in

polypropylene, these bands at 974 cm.^{-1} and 995 cm.^{-1} have a highly desirable profile for the quantitative determination of isotactic/atactic ratio. It will be shown that the ratio of their intensities can be used to determine the degree of isotacticity in a sample.

At this point however, it would be appropriate to discuss the terms "isotacticity" versus "crystallinity" as they are used here. It is unfortunate that the spectrum of atactic polypropylene is nearly identical with that of molten (or amorphous) isotactic polypropylene. This means that it is difficult to distinguish in the infrared between the atactic and amorphous isotactic polymers. This leads to confusion about what is actually measured when an attempt is made to determine either isotacticity or crystallinity by infrared.

In Figure 3B the 1050-cm.^{-1} to 775-cm.^{-1} region was recorded at intervals (under nitrogen) while the 100% isotactic sample was cooling from 180°C . One can follow the onset of crystallization by noting the increasing intensity of the 995-cm.^{-1} band in comparison to the band at 974 cm.^{-1} while cooling. In Figure 3C is shown a set of spectra of samples of various isotactic content. As one would expect this shows that isotactic content and crystallinity are closely related.

Our data on the isotactic/atactic ratio are based on standard samples prepared from isotactic and atactic starting material. Therefore, the isotacticity rather than the absolute crystallinity has been measured.

Of course, the degree of crystallinity in these samples will effect the results of the isotacticity measurements since the same spectral changes occur with variation in crystallinity as occur with variations of isotacticity. We have found, however, that this difficulty is a minor one, since crystallinity does not vary significantly with sample preparation.

It has been found, for example, that when a known 60% atactic sample is quenched from the melt to liquid nitrogen temperature (-196°C .) or slow-cooled (7 hr.) from the melt, the apparent atactic content becomes 69% and 50%, respectively. However, the apparent atactic content returns to approximately the original amount upon aging for a week. Generally speaking, it is a knowledge of the isotactic content that is required. Therefore the standards that the infrared method is based on, were prepared over a reproducible 45-min. cycle. This time period was considered to be approximately the time period that commercial samples would undergo when molded under normal

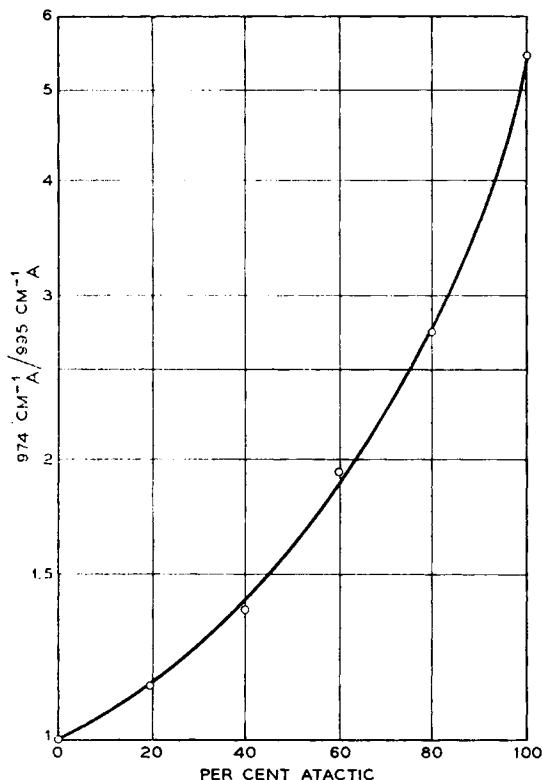


Fig. 4. Analytical curve for determining atactic content of polypropylene.

conditions. This keeps the degree of crystallinity uniform and relevant and determines the isotacticity rather than crystallinity as such.

Returning to the development of the infrared method, the standards were prepared by placing known amounts (w/w) of 100% atactic and 100% isotactic materials in a test tube into which nitrogen was passed. The test tube was then immersed in a silicone oil bath and heated to 210°C . The mixtures were thoroughly stirred and then cooled. The entire cycle (i.e., heating, mixing, cooling, and molding) took approximately 45 min. The infrared spectra of the standards were recorded, and the intensity ratios of the 995-cm.^{-1} and 974-cm.^{-1} bands of each standard were determined. With these values a working curve for the atactic content, from 0% to 100% was plotted. The working curve is shown in Figure 4.

The accuracy of the method is estimated to be $\pm 2\%$ over the 0-100% range. However, if one were interested in better accuracy in a particular range, say, in the 0-10% atactic range, appropriate standards could be made and a curve prepared for this range.

A significant advantage of the infrared method is the speed with which it can be performed. Using

this method, the atactic content of a sample can be determined in approximately 45 min. as compared to 2 to 3 days for the extraction method.

Since the sample is merely molded into a film for the infrared method, it is not likely that the molecular weight distribution is of any concern nor is the physical nature of the sample. However, the extraction method requires the sample to be in the form of a fine powder which is often difficult to achieve with polymeric materials. Also, the molecular weight distribution is a factor to be considered since it is evident that some of the low molecular weight fractions are extracted along with the atactic material.

Determination of Oxidation Products

The formation of oxygen-containing degradation products was followed by recording the infrared spectra of isotactic polypropylene during accelerated oxidation. The oxidation runs were made while heating a sample of isotactic polypropylene in air at 150°C. Oxygen was not used as in the polyethylene study,⁷ since polypropylene with its numerous oxidation-susceptible tertiary carbons oxides much more quickly than polyethylene.

The first region of interest is the 4000–3000 cm^{-1}

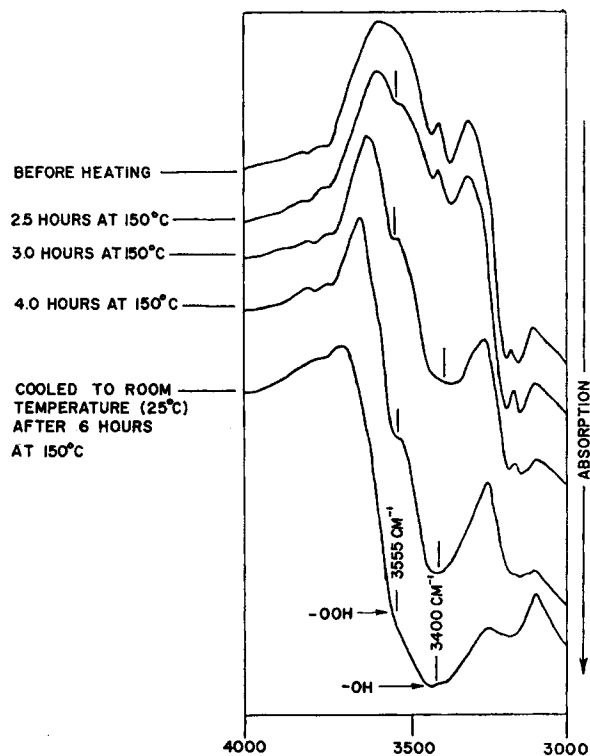


Fig. 5. The OH-stretching region of polypropylene during and after accelerated oxidation.

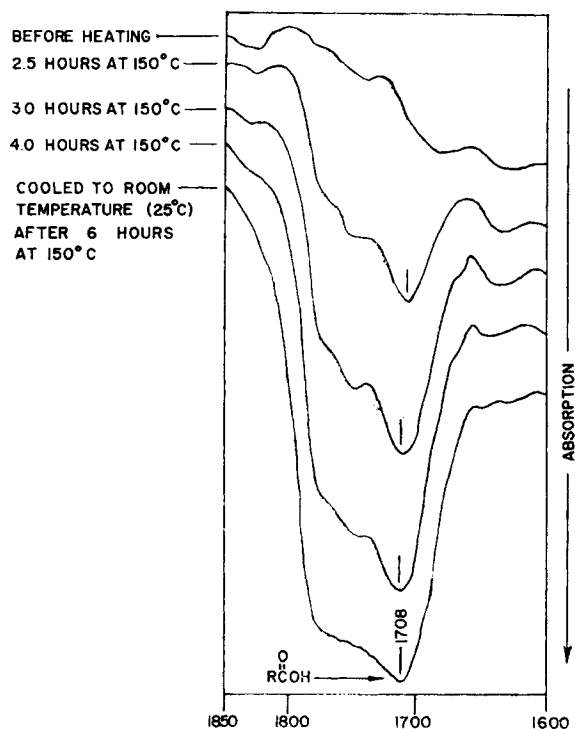


Fig. 6. Carbonyl region of polypropylene during and after oxidation at 150°C.

OH-stretching region. After 2.5 hr., the band near 3400 cm^{-1} began to broaden toward 3550 due to the formation of hydroperoxide groups which absorb at 3555 cm^{-1} .⁷ This 3400- cm^{-1} band continued to broaden toward 3550 cm^{-1} and then also began to increase in intensity. This hydroperoxide band at 3555 cm^{-1} did not resolve itself as it did in the polyethylene oxidation study.⁷ Upon further heating, both these bands continued to increase and finally merged into a broad and strong absorption as shown in the bottom trace of Figure 5.

It is interesting to note that the —OH band at 3400 cm^{-1} continued to increase steadily during oxidation with no significant increase after cooling, whereas the polyethylene —OH band, under similar conditions, increases only slightly during oxidation but upon cooling increased strongly.

The carbonyl region, from 1850 to 1650 cm^{-1} , is shown in Figure 6. For the first 1.5 hr. there was no indication of carbonyl-containing products being formed. Then after 2.5 hr. they rapidly began to form. From this point on, the formation of oxidation products proceeds quite rapidly in comparison to polyethylene under comparable conditions. Although the typical —C=O bands due to aldehydes, esters, and ketones were merged into a single, broad, ill-defined band between 1710

and 1750 cm.^{-1} , the band for acid —C=O near 1708 cm.^{-1} was quite distinct. This acid —C=O was the first to form and remained the strongest during and after oxidation, showing the acid groups to be one of the major oxidation products of polypropylene. As in the case of the hydroperoxide-hydroxyl band, the various bands due to the different types of carbonyls did not resolve themselves as well as those of polyethylene. The band continued to increase in intensity but remained a broad absorption with no character except for the acid —C=O at 1708 cm.^{-1} .

This apparent lack of resolution of the OOH/OH and —C=O bands, as compared to similar bands in oxidizing polyethylene, indicates that a larger variety of hydroxyl- and carbonyl-containing structures are formed in polypropylene. A broad band is what one would expect from a large variety of structures, since there would be a greater number of absorptions in their respective regions that would tend to overlap and mask each other resulting in a broad, ill-defined band.

Unsaturation

In a preliminary observation of the atactic spectrum, it was noted that the profile and location of the 974-cm.^{-1} band is somewhat similar to a *trans* ethylenic-type unsaturation band, but the intensity indicated more unsaturation than is normally considered to be in polypropylene. Also, a weak band was observed at 888 cm.^{-1} which could be attributed to a pendant-type unsaturation ($\text{R}_1\text{R}_2\text{C=CH}_2$). The sample was subjected to extensive chlorination in order to eliminate any unsaturation. After chlorination, the strong band at 974 cm.^{-1} did not diminish, but the weak band at 888 cm.^{-1} disap-

peared, showing that the former band is not due to unsaturation but the latter band is. Figure 7 shows the $1050\text{--}875\text{ cm.}^{-1}$ region before and after chlorination. The weak intensity of the 888-cm.^{-1} band indicates only a small percentage (1% or less) of pendant-type unsaturation in the sample

SUMMARY

Through comparison of the infrared spectra of "100% isotactic" and "100% atactic" polypropylene, the absorption bands due to the isotactic and atactic phases have been determined.

A method for determining isotacticity is proposed which is based on the atactic and isotactic sensitive bands. It is independent of the physical nature of a submitted sample, the molecular weight distribution, and minor constituents such as stabilizers, etc. This method is more rapid and is believed to be more reliable in view of the nature of the extractable matter from the presently used extraction method.

The difficulty arising from the identity between the spectra of the atactic and molten amorphous isotactic material has been overcome by making standards from mixtures of known atactic and isotactic materials. The method therefore measures isotactic content rather than absolute crystallinity.

In the process of oxidation, it is evident that polypropylene, with its numerous tertiary carbon atoms, produces more carbonyl- and hydroxyl-containing degradation products and oxidizes more rapidly than polyethylene. As a result the transition point from the induction state to the autocatalytic phase is more abrupt than that found in polyethylene.

Finally, the type of unsaturation in polypropylene has been ascertained to be of the pendant type ($\text{R}_1\text{R}_2\text{C=CH}_2$) and is in the order of 1%.

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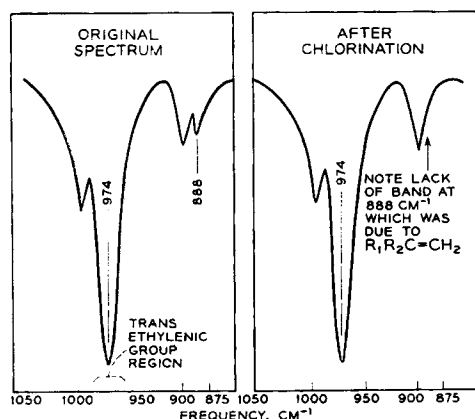


Fig. 7. Infrared spectra of commercial atactic polypropylene before and after chlorination.

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Synopsis

The structural configurations that distinguish the atactic phase from the isotactic phase give rise to infrared spectra characteristic of each phase. Since these differences are quite significant, a method is proposed with which the isotacticity can be determined. The relation between the isotactic phase and crystallinity is considered, and its application to this study is discussed. The formation of oxygen-containing degradation products was followed during accelerated oxidation and the products identified. There is also evidence that more numerous oxygen containing degradation products form in polypropylene than in polyethylene. The type of unsaturation was also determined, and its presence confirmed by chlorination.

Résumé

Les configurations structurales qui distinguent les phases atactiques des isotactiques engendrent aux infrarouges des spectres caractéristiques de chaque phase. Depuis que ces différences ont leur sens, on a proposé une méthode pour déterminer l'isotactisme. La relation entre la phase isotactique et la cristallinité a été regardée et son application à

cette étude est discutée. La formation de produits de dégradation renfermant de l'oxygène a été suivie pendant l'oxydation rapide et les produits ont été identifiés. Il est aussi évident que les produits de dégradation renfermant de l'oxygène sont plus nombreux dans le propylène que dans le polyéthylène. Le type de non-saturation a été aussi déterminé et sa présence déterminée par chloration.

Zusammenfassung

Die Konfigurationsunterschiede in der Struktur einer ataktischen und einer isotaktischen Phase geben auch Anlass zu Infrarotspektren, die für jede Phase charakteristisch sind. Da diese Unterschiede recht augenfällig sind, ist es möglich eine Methode zur Bestimmung der Isotaktizität anzugeben. Die Beziehung zwischen der isotaktischen Phase und der Kristallinität wird untersucht und ihre Anwendung auf das vorliegende Problem diskutiert. Die Bildung sauerstoffhaltiger Abbauprodukte wurde während der beschleunigten Oxydation verfolgt und die Produkte identifiziert. Es bestehen auch Hinweise dafür, dass im Falle des Polypropylens eine grössere Anzahl von sauerstoffhaltigen Abbauprodukten entsteht als beim Polyäthylen. Auch der Typus der ungesättigten Produkte wurde bestimmt und ihre Gegenwart durch Chlorierung bestätigt.

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